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Electrochemistry of Main-Group Phthalocyanines

A. B. P. Lever* and P. C. Minor

Received February 5, 1981

Metallophthalocyanines have been the subject of several electrochemical investigations,¹⁻⁹ but no systematic study as a function of central metal ion has been published. We have recently completed a study of the electrochemistry of main-group phthalocyanines with a view of providing a basis for the design of photoredox catalysts. Differential-pulse polarography and cyclic voltammetry were employed to identify the energies of the various redox couples. We are concerned here with the first ring reduction and first ring oxidation. For most couples, these processes were reversible or quasi-reversible in the medium (DMF/TEAP) employed.

A well-defined relationship was observed between the first ring reduction, or oxidation, and the size and charge of the central metal ion. This information is of special value of those interested in the potential use of phthalocyanines as photocatalysts.

Experimental Section

The main-group metallophthalocyanines were prepared and purified by well-established literature methods.¹⁰ Electrochemical data were recorded with Princeton Applied Research Models 173, 174A, 175, a Houston Model 9002A XY recorder, and Tektronix 5103N storage oscilloscope. A standard calomel electrode was used as a reference (with Luggin capillary) and platinum wire used as working and counterelectrodes. Dimethylformamide (Fisher, "Spectranalysed"), and tetraethylammonium perchlorate (Eastman, recrystallized several times) were used as solvent and supporting electrolyte, respectively. Details of our electrochemical procedures have been previously published.³

Discussion

Redox couples for a range of main-group metallophthalocyanines are shown in Table I. A well-defined pattern is readily apparent. (i) The metal phthalocyanines with the more positive central metal ions are more difficult to oxidize. (ii) The phthalocyanine anions with the more positive central metal ions are more difficult to oxidize, i.e., their neutral species are easier to reduce. (iii) From comparison of the dipositive or tripositive ions, the smaller the ion, the easier is the species to reduce, and the more difficult to oxidize. (iv) Elements with especially large radii, specifically lead and mercury, have anomalous redox energies; these ions presumably sit outside the phthalocyanine ring and do not then fit into the well-behaved series of complexes.

Observations i-iii lead to the supposition that these redox energies are functions of the polarizing power of the central metal ion, expressible as charge/radius (ze/r). Increasing polarizing power of the central metal ion causes an increase in the potential at which the phthalocyanine or phthalocyanine anion is oxidized.

There are a variety of metal ion radii available in the literature. We have chosen to use the effective ionic radii of Shannon and Prewitt¹¹ because their list contains a fairly complete set of radii shown as a function both of valency and coordination number.

The coordination numbers of these species are not unambiguously known, but it is likely that most of the complexes will be solvated to form six-coordinate derivatives in solution in DMF.

Since these main-group species are all closed-shell ions, we have used the formal charge ($2+$ or $3+$) to generate (ze/r) values shown in Table I.

A plot of these quantities, E° vs. ze/r , is curved. A linear plot is conveniently obtained by plotting E° against (r/ze) and

is shown in Figure 1 for both phthalocyanine reduction and oxidation. The linearity of both plots is striking. The equations of the lines are as follows: oxidation, $(ze/r)(E^\circ - 1170) = -11.7$; reduction, $(ze/r)(E^\circ + 385) = -12.0$. E° is relative to the standard calomel electrode.

Table I. Main-Group Phthalocyanine Reduction and Oxidation Couples (mV vs. SCE)

metal	radius, pm	ze/r	$E^\circ_{\text{Ox}},^a$ mV	$E^\circ_{\text{Red}},^a$ mV	$E^\circ_{\text{Ox}} - E^\circ_{\text{Red}},$ mV
(O ³⁺ Am) ₂ Si ^{IV}	54	0.074		-540	
ClAl ^{III}	67.5	0.044	915	-655	1570
ClGa ^{III}	76	0.040	865	-735	1600
ClIn ^{III}	94	0.032	830	-715	1545
Mg ^{II}	86	0.023	650	-930	1580
Zn ^{II}	88	0.023	685	-900	1585
Cd ^{II}	109	0.018	540	-1170 ^b	1710
Hg ^{II} ^b	110	0.018	250	-1305	1555
Pb ^{II} ^b	133	0.015	670	-720	1390

^a Potentials quoted to nearest 5 mV. ^b These data were not included in the derivation of the equation of the line. Where previous data exist, agreement is satisfactory.^{1,9}

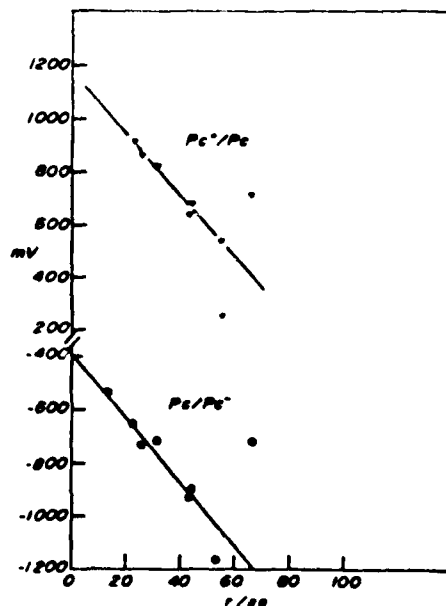
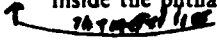


Figure 1. Main-group phthalocyanine oxidation and reduction potentials plotted as a function of r/ze . Points lying off the lines are for the large ions Pb(II), Hg(II), and Cd(II) (reduction only) which do not lie within the phthalocyanine ring.

Although the least-squares plots do not show that the lines are strictly parallel, the deviation therefrom is small. For most species the difference in potential between ring reduction and oxidation is close to 1570 mV.

Provided that the metal ion sits inside the phthalocyanine ring, these correlations provide a method of estimating main-group phthalocyanine redox potentials. Interestingly, the limit of phthalocyanine oxidation and reduction appears to be +1170 and -385 mV (vs. SCE), respectively, as (r/ze) approaches 0. All main-group phthalocyanines should fall within these confines, provided  inside the phthalocyanine ring.


Successive oxidation and reduction potentials (e.g., second and third reductions) can be estimated from the established intervals between these various processes.⁴

Transition-metal phthalocyanines follow a similar trend.^{5,12} For a given valency where, within the first-row transition series the size of the metal ion does not change greatly, the reduction potential depends upon the valency. Thus Cr(II), Mn(II), Ni(II), and Cu(II) phthalocyanines all reduce at essentially the same potential (ca. -0.84 vs. SCE) anodic of M(I) species such as Fe(I) and Co(I) and cathodic of M(IV) species such as TiO and VO.¹²

The use of these data in the design of photoredox catalysts will be the subject of a future communication.¹³

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